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16. ABSTRACT

Particulate reference samples have been prepared for the standardization of X-ray fluorescence spectrometers used in the analysis of air particulate matter. Uniform layers of reground orchard leaves of known composition, i.e., National Bureau of Standards Standard Reference Material 1571, were deposited on membrane filters and coated with a thin polymer film for protection against abrasion and moisture. These samples have been prepared with mass per unit area of 0.1 to 5.0 mg/cm^2.

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I

INTRODUCTION

Within the past several years, an increasing number of x-ray analyses of environmental and biological samples have been reported in which the National Bureau of Standards Standard Reference Material (SRM) 1571 orchard leaves was used as a trace element calibration standard [1-3]. This botanical SRM is well suited to such applications because it contains a number of trace elements such as S, Cl, K, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, As and Pb which are important in the analysis of environmental samples. In the analysis of ambient air particulates, the sample analyzed is often in the form of thin deposits on either membrane or Whatman type filters. Therefore, it is desirable to have a calibration sample in the same form. The preparation of orchard leaf deposits on membrane filters to be used for this purpose is described in this report.

The NBS SRM as certified requires that at least 250 mg samples be taken to insure that the trace element distribution is representative of the bulk material. To permit smaller samples to be used and to minimize the attenuation of x-rays in the individual particles, the material was reground. A number of different coatings were investigated to provide good sample protection, and at the same time obtain low attenuation of the x-rays from elements such as phosphorus and sulfur. Different coating materials that were investigated consisted of polyisobutylene, heat-sealed overlays of polypropylene and Parafilm, and vapor-deposited Parylene films.

EXPERIMENTAL

Sample deposits were prepared by filtration of a suspension of the reground material in cyclohexane. Attempts were made to prepare deposits from an aerosol suspension, but were not successful.

A. Grinding of the Orchard Leaves SRM 1571

A high velocity air impact grinder was used to reduce the particle sizes. The impactor produces two size fractions having relatively broad size distributions. The "fines" fraction was collected after each pass through the grinder and was reground four times. The particle size distribution of the collected material was characterized by automated image analysis. Data were taken by examining nine regions of four different sample preparations. These samples were prepared by dispersing a few milligrams of material in cyclohexane with ultrasonic stirring. About three drops of this suspension were placed on a microscope slide, covered with a cover glass and allowed to dry.

B. Preparation of Deposits on Membrane Filters

From 2 to 15 mg of dried reground orchard leaves were weighed and transferred to a 50 ml beaker containing about 40 ml of spectrograde cyclohexane. The beaker containing the orchard leaves was placed in an

ultrasonic bath for about one minute to disperse the particles. The suspension was transferred to a vacuum filtering unit and the sides of the beaker were washed down with cyclohexane. The material was filtered rapidly through a 37 mm preweighed membrane filter (0.8 μm pore size). The glass filtering funnel was constructed so that deposits on the 37 mm membrane filters were 29 mm in diameter. The net weight of the air-dried deposit was used to calculate the areal density of the deposit in mg/cm^2. All weighings were performed in a room in which the relative humidity was maintained at 50±4 percent.

C. Preparation of Parylene-Coated Samples

The samples were coated at the Union Carbide Corporation with a thin film of Parylene N — a polymeric material developed by Union Carbide Corporation (U.S. Patent No. 3342754). The procedure consists of first vaporizing the di-para-xylylene dimer by heating it at 175°C at 760 mm Hg (1.01×10^5 N/m^2). This vaporized material passes through a deposition chamber maintained at room temperature, and 0.1 mm Hg (13.3 N/m^2) which contains the samples to be coated. The samples are rotated in the chamber to insure a uniform coating of Parylene. The exit of the deposition chamber is connected to a cold trap (-70°C) and pumped with a mechanical pump to a pressure of 0.001 mm Hg (0.133 N/m^2). The film thickness is monitored in the deposition chamber using a piezoelectric frequency sensor. More accurate thickness measurements were made at Union Carbide after removal of the samples using a UV spectrophotometer. The thickness is calculated from a calibration curve by comparing the absorbance of the film with that of a film of known thickness measured interferometrically.

D. Preparation of Thin-Film Overlays of Parafilm and Polypropylene

A sheet of Parafilm (American Can Co.) was stretched by hand as thinly as possible without causing the sheet to tear, and was placed directly on the sample which was held by suction to a filtering funnel. A polypropylene sheet (0.08 mm thick) was next placed on top of the Parafilm and was heat-sealed to the sample using a hot air gun.

E. Mounting the Parylene-Coated Filter Deposit

Filter holders for mounting the deposits were supplied by EPA, and are described in an EPA report [4]. These holders, designed to accommodate 37 mm diameter membrane filters, were modified by increasing the platform diameter by 2 mm. This permitted the filter deposit to be centered in the holder more easily and also allowed for some expansion of the membrane filter before cementing in the holder. The filter deposit was held on a filtering funnel by applying suction. A thinned mixture of cement prepared by mixing equal parts of Barge all-purpose cement, ethyl acetate and cyclohexane was brushed on the platform of the holder. The filter was cemented to the holder platform by pressing the holder flat against the outer edge of the filter deposit and then allowed to dry.

RESULTS AND DISCUSSION

Neutron activation analysis (NAA) of the reground orchard leaves showed that the concentrations of iron, nickel, cobalt and chromium were much higher than in the certified SRM 1571. Therefore, it was important to determine if these introduced elements were homogeneously distributed throughout the material. For this reason, sixteen samples of reground material (200 mg each) were taken and six elements, including iron and chromium, were analyzed by NAA. An analysis of variance of these concentrations in the material indicated that there were no gross inhomogeneities (not greater than five percent). These results indicated that the reground SRM 1571 was satisfactory for use provided that recertification of the introduced elements could be accomplished. An analysis of a number of these elements using NAA, atomic absorption spectrophotometry (AAS), and photon activation analysis (PAA) are included at the end of this report. Further work on the analysis of this material is still in progress.

The particle size distribution of the reground material is shown in figure 1. The area of about 80 percent of the 3000 particles examined was between zero and 7.5 μm^2 (3.1 μm equivalent diameter). Less than 0.5 percent of the particles were within 82.5 and 105 μm^2, with no particles observed above 105 μm^2.

To determine if the cyclohexane treatment altered the trace element composition of the orchard leaves, NAA was performed on cyclohexane extracts and on the material after treating with cyclohexane. A number of elements, including Br, Mn, Fe, K and Na, were analyzed. The results showed that only sodium was affected by this treatment, and about 50 percent was extracted.

A simple technique was developed for measuring the uniformity of the deposits. This consisted of directing a laser beam about 2 mm in diameter normal to the sample, and measuring the intensity of the light transmitted [5]. Using a Beer's law calibration of absorbance vs areal density, the uniformity of the deposit was measured. Of the several samples examined having areal densities of 1.0 to 2.0 mg/cm^2, variations in uniformity did not exceed 0.02 mg/cm^2.

A number of coating materials were investigated and compared with regard to their ability to adhere to the sample and to provide protection from abrasion and humidity. These consisted of vapor-deposited Parylene films and heat-sealed overlays of polypropylene using Parafilm as a binder. Also, orchard leaf deposits were prepared from suspensions in cyclohexane containing from 0.1 to 10 percent by weight of polyisobutylene. Another important factor considered was the x-ray attenuation of these coatings, especially from elements of low atomic number such as phosphorus and sulfur. The attenuation of P, S, K, and CaKα lines was measured by comparing the background corrected peak intensities of coated and uncoated samples having the same areal densities using a wavelength-dispersive x-ray spectrometer.

The values obtained for various thicknesses of Parylene and of thin polypropylene and Parafilm coatings are summarized in tables 1 and 2, respectively. For Parylene coatings 75 to 193 nm thick, little change in attenuation was noted. Also, the x-ray background intensities from these samples were essentially the same as the uncoated samples except that the background of the 2500 nm thick sample was increased significantly. The attenuation values of the polypropylene-Parafilm coatings could not be reduced any further because thinner films were not available. In order to produce adherent deposits using polyisobutylene, as much as one percent or greater by weight of the polymer in cyclohexane was used. However, the amount of polyisobutylene retained on the samples varied considerably making it difficult to obtain reproducible attenuation data. For this reason, this coating material was considered unsatisfactory.

Table 1. Average Attenuation Values of Parylene Coatings[a]

sample areal density = 2.0 mg/cm^2

No. of Samples	Parylene Thickness, nm	Percent Attenuation Element	Average	S^b
5	75	P	3	1.7
3	75	S	2	1.3
2	75	K	1.4	--
5	117.5	P	3.1	0.50
5	117.5	K	1.7	0.44
5	158.0	P	5.4	0.90
2	158.0	S	5.2	--
4	158.0	K	2.9	0.35
7	166.5	P	5.0	0.81
5	166.5	S	4.3	0.92
7	166.5	K	2.6	0.69
5	193.0	P	7.3	0.88
3	193.0	K	3.7	0.20
3	2500	P	33	1.5
3	2500	S	28.9	0.71
2	2500	K	11.4	--

[a]Calculated from the expression $I_u - I_c / I_u \times 100$; where I_u = peak intensity of uncoated sample, and I_c = peak intensity of coated sample.

[b]S = standard deviation of a single measurement.

Table 2. Attenuation Values of Polypropylene and Parafilm Coatings

Sample #	Total Coating Thickness, mg/cm^2	Percent Attenuation P	S	Cl	K	Ca
1	1.2	28.1	23.2	14.1	10.9	8.5
2	1.1	24.4	23.6	16.2	11.4	7.9
3	1.2	26.3	24.4	13.6	10.1	8.3
Average		26.3	23.7	14.6	10.8	8.2

The ruggedness of samples coated with Parylene films (75 to 200 nm thick) were tested by an air jet which impinged on the sample surface. Effects of humidity were observed when the samples were placed in a chamber maintained at 100 percent relative humidity.

The trace element composition of the starting material (di-para-xylylene dimer) was analyzed at Union Carbide Corporation. Of the 27 elements analyzed, sodium, magnesium, iron and aluminum were present in concentrations from 2 to 9 ppm. Silicon was 31 ppm, and the remaining elements were either below 1 ppm or were not detected. These results indicate that the Parylene material should be of sufficient purity for application in this work. Since the Parylene films appeared to furnish good sample protection, including high resistance to humidity, high purity, good adherence, and acceptable x-ray attenuation for the low atomic number elements, 60 samples were prepared and delivered to EPA containg from 0.1 to 5.0 mg/cm^2 of orchard leaves coated with 117.5 nm of Parylene.

A photograph of a typical reference sample mounted in a holder is shown in figure 2.

Table 3. Preliminary Results of the Analysis of Reground SRM 1571 Orchard Leaves

Element	No. of Meas.	Average, μg/g	Rel. Std. Dev. %	Certified Values of SRM 1571, μg/g
Fe[a]	3	791	0.2	300±20
Ni[a]	3	22.5	0.5	1.3±0.2
Ni[b]	1	21.5	---	
Cr[c]	15	41.97	3.70	(2.3)
Mn[c]	16	102.1	1.84	91±4
K[c]	16	1.49 (wt. %)	1.53	1.47±0.03 (wt. %)
Br[c]	15	10.48	2.58	(10)
Zn[c]	15	24.99	3.22	25±3

[a] = AAS

[b] = PAA

[c] = NAA

Values in parenthesis are not certified.

II

CONCLUSIONS

Reference samples consisting of uniform layers of reground orchard leaves of known composition, i.e., NBS SRM 1571, on membrane filters were prepared for the standardization of x-ray fluorescence spectrometers. These samples have areal densities of 0.1 to 5.0 mg/cm^2, and are coated with a thin polymer film for protection against abrasion and moisture.

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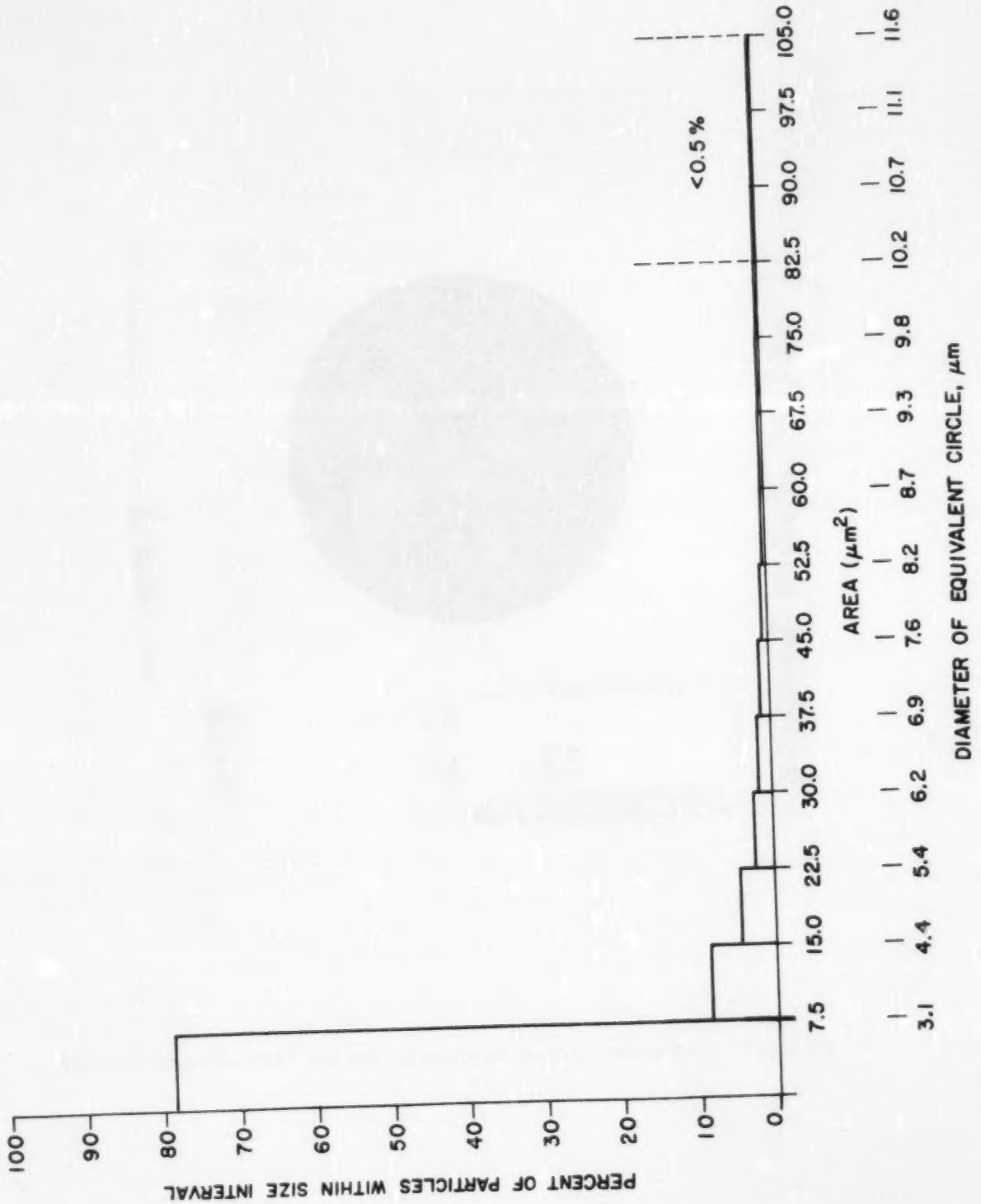

Figure 1. Particle size distribution of orchard leaves.

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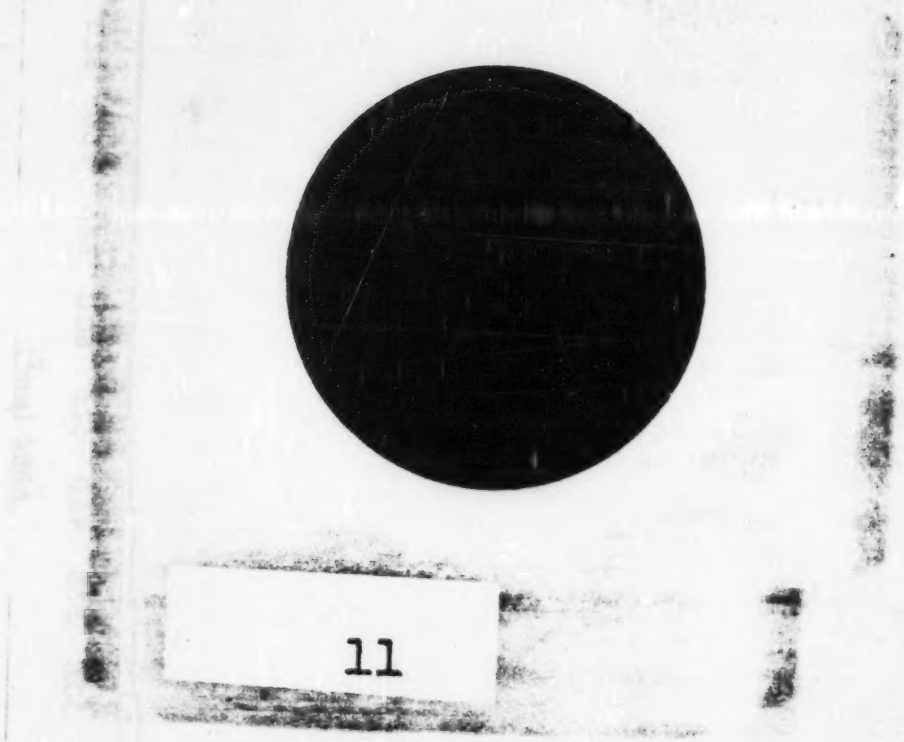

Figure 2. Reference sample mounted in holder (actual size 5x5 cm).